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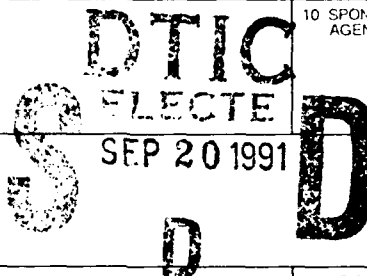
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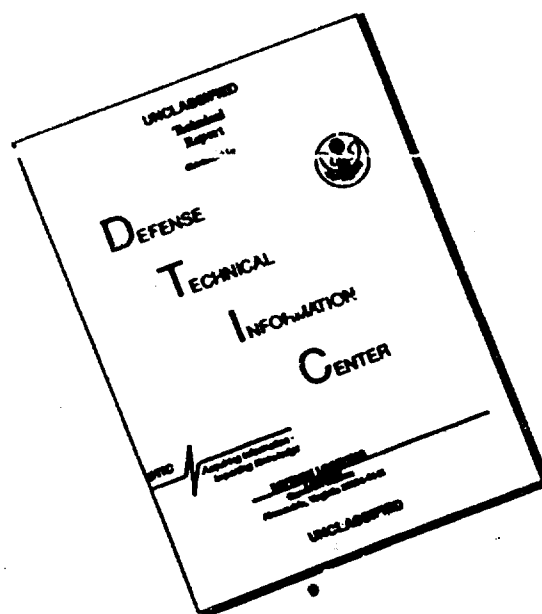
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Synthesis of Diamond Films with Pulsed Plasmas

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Diamond films were grown in plasmas formed with microwaves that were modulated with a pulse generator. Films obtained with the use of pulse periods in the nanosecond, microsecond, and millisecond ranges were compared to baseline films which were obtained with CW microwaves. The deposited films were examined with SEM, XRD and Micro-Raman spectroscopy. For the experimental conditions used, the diamond films' growth rates and quality improved with increasing pulse duration while maintaining a duty cycle at nearly 50 percent, and reached a maximum with CW generated films. This was attributed primarily to an increasing plasma on-time which resulted in a corresponding increase in the atomic hydrogen partial pressure at the growth surface.

I. INTRODUCTION

The metastable growth of diamond films has been achieved by a number of continuous plasma-enhanced chemical vapor deposition (CVD) methods [1-4]. Of these, none have gained more attention than the CW microwave plasma-enhanced chemical vapor deposition technique [4]. In this technique the amount of microwave power used is typically limited by the extent of substrate heating induced by plasma and microwave heating. Concomitantly, this restriction in the amount of microwave power that can be used also reduces the amount of reactants that can be dissociated which may adversely effect the film's growth rate as well as quality.

The use of pulsed radio-frequency discharges of very high power to deposit thin films has recently been reported by Scarsbrook et al. [5]. They found that short pulses at high power resulted in increased reactant dissociation rates while simultaneously reducing substrate heating. This resulted in higher deposition rates at lower temperatures than previously obtained under CW conditions. In this paper we investigate the use of microwave induced pulsed plasmas in the CVD growth of diamond films.

II. EXPERIMENTAL PROCEDURE

A microwave plasma-enhanced CVD system with a dielectric waveguide was used in the deposition of the diamond films. A schematic of the system used is shown in Figure 1. The use of dielectric waveguides to form plasmas has been described previously [6]. The microwave supply was modified by the addition of a Phillips PM5715 pulse generator for pulse operation, and the maximum power output was increased by an order of magnitude to 2.5KW at 7.36 ± 0.050 GHz from that previously reported, with the use of an Energy Systems 2.5KW, Low X-Band Amplifier.

Deposition was performed on (100) silicon n-type substrates. To aid in the nucleation and reduce the time necessary to nucleate the diamond film, the substrates were seeded by abrading them with diamond crystals that were up to 2 micrometers in size. The dielectric waveguide, located within the inner chamber, is maintained at atmospheric pressure. The silicon substrates were placed horizontally on sapphire tiles that rested on the inner chamber just above the output end of the dielectric waveguide. In addition Grafoil, a graphite sheet product of EGC Corporation, was placed about the substrate. These procedures were used to suppress unwanted plasma reactions and minimize any potential contamination of the diamond film.

After the deposition tube was evacuated to less than 100 millitorr, argon was introduced into the reaction chamber and the plasma initiated when the pressure was about 5 torr. Oxygen, and then hydrogen were introduced into the reaction chamber. An average deposition pressure of 5 torr was first set by using a throttle valve, and then adjusted with a vernier controlled metering valve. The plasma's intensity was greatest at the surface of the substrate and decreased with distance from the surface. Depositions were performed with and without the use of external heating. When a furnace was not used the substrate was heated only by the plasma and microwave heating. Substrate temperatures were measured with a Chapin Tec, Model ROS-5U two color optical pyrometer. The temperature deposition range was between 800 and 1050°C with an average substrate temperature of 925°C.

The gas flow rates during deposition were 100 cc/min hydrogen, 0.5 cc/min methane, and 0.5 cc/min oxygen. In addition argon, which acted as a diluent, was added to the gas flow in the amounts of 100 cc/min for CW and 50 cc/min for pulsed-plasmas depositions respectively. The pulse generator was run in the nanosecond, microsecond, and millisecond ranges. The Energy Systems klystron amplifier was set to obtain the system's peak power for all pulsed-plasma depositions. Duty cycles were adjusted, at about 50 percent, to obtain an average forward power that was similar to the power used in CW baseline depositions. An effort was made to maintain the substrate at a deposition temperature similar to that of the CW baseline. Deposition times were between 7 and 8 hours.

III. RESULTS

Some remarks are in order concerning the pulsing of microwaves and the resulting plasmas. Plasmas formed with pulse repetition rates in the nanosecond range were continuous. Plasmas formed in the microsecond and millisecond ranges were pulsed. In addition, the the rise and fall time of the microwave system was approximately 40 nanoseconds, primarily due to the narrow bandwidth of the klystron amplifier. As a result, in nanosecond pulsed experiments the peak microwave power was not reached during the pulse on-time nor was the microwave power completely turned off during the pulse off-time.

In the nanosecond range, with a pulse duration and repetition time of 54 and 100 nanoseconds respectively, the deposited film was not continuous. An SEM micrograph of the discrete crystallites, with poorly defined faceting, is shown in Figure 2a. With the pulse duration and repetition time increased to 5 and 10 microseconds respectively, the deposited film exhibited mostly (111)

faceting as can be seen in Figure 2b. Facets, primarily the (111), were reasonably formed and typically submicrometer in size. However, some of the (100) facets were found to be 2.5 micrometers in length. The average deposition rate was 0.4 micrometers per hour. In the millisecond pulsed- plasma range, with a 5.6 millisecond pulse duration and a 10 millisecond repetition time, the film exhibited well defined (111) and (100) facets. An SEM micrograph is shown in Figure 2c. The largest (100) facet faces measured 5 micrometers in length. The average deposition rate was 0.8 micrometers per hour. For comparison purposes a CW plasma baseline film was deposited. The power used was equal to half of the peak power used in the pulsed mode. The SEM micrograph of this film is shown in Figure 2d. As can be seen very well defined (100) and (111) facets are present. The largest (100) facets faces measured 12 micrometers in length. The average deposition rate was 1.5 micrometers per hour.

If we assume that diamond seeding reduces or eliminates the incubation period the average growth rate may be determined from the thickness of the film and the time of deposition. In Table 1, the thickness and growth rate of the deposited films is shown as a function of the pulse period. For the method chosen to calculate the growth rate, i.e., based on film thickness, no growth rate could be assigned to the non-continuous film grown with the plasma generated with nanosecond pulsed microwaves. As can be seen, the thickness of the deposited films by the pulsed- plasma technique increased with the pulse period and reached a maximum with CW plasmas.

Table 1. Thickness and growth rates of pulsed and CW plasma deposited films.

| MICROWAVE POWER | FILM THICKNESS (μm) | FILM GROWTH RATE ($\mu\text{m/hr}$) |
|------------------------|----------------------------------|---------------------------------------|
| nsec PULSED | NON-CONTINUOUS | — |
| μsec PULSED | 2.5 | 0.4 |
| msec PULSED | 6.0 | 0.8 |
| CW | 10.2 | 1.5 |

A Rigaku Rotaflex RU 200B X-ray diffractometer was used to determine the structure and nature of the deposits. X-ray diffraction patterns of the continuous deposited films obtained with plasmas formed with microsecond and millisecond pulsed, and CW microwaves are shown in Figure 3. Stick figures of the standard powder pattern of natural cubic diamond are also shown. These define the location and relative intensity of the most prominent cubic diamond crystallographic planes, i.e., (111), (220), (311), (400), and (331) within the diffraction angle of 2 theta that lie between 0 and 140 degrees. The sharp peaks not located at the stick figures are that of the crystalline (100) oriented silicon

substrate. Of particular interest is the deviation between the standard powder pattern stick figures relative intensity ratios and that of the intensity ratios of the deposited diamond films. These differences indicated that the deposited diamond film crystal orientation is non-random and exhibits a preferred texture.

The Raman spectra of continuous films deposited with plasmas formed with microsecond and millisecond pulsed, and CW microwaves were generated by Instruments SA on their Raman Microprobe S3000 spectrophotometer and are shown in Figure 4. Excitation was provided with the 514.5 nm line of an argon ion laser. The film grown with the microsecond pulsed plasma exhibits a very broad non-diamond peak about 1600 cm^{-1} above a fluorescent background. The msec pulse film shows a broad diamond peak about 1332.4 cm^{-1} and a broad non-diamond peak about 1500 cm^{-1} . By comparison, the Raman spectrum of the baseline CW plasma film exhibited a sharp diamond peak with a FWHM of 5.5 at 1333.5 cm^{-1} with no other carbon peaks or fluorescent background present. Sharma et al. [7] found that differences in diamond Raman peak location could be attributed to strain in the diamond.

The pulsed-plasma average power levels were nearly equal to those used in the baseline CW plasma, however, the use of pulsed-plasmas with long pulse off-times can result in reduced heating of the substrate. Although this study did not specifically address the optimization of temperature, to determine if a temperature effect did exist with pulsed-plasma depositions, the substrates were heated to 600°C before the plasma was ignited. A less than ten percent improvement in film thickness for the microsecond pulsed-plasma case indicated some substrate cooling had occurred. In this case the deposition temperature could have been optimized for maximum growth, but it was not the primary cause for the lower growth rate.

IV. DISCUSSION

Our present understanding of the chemical vapor deposition of metastable phases, such as diamond, is that large deviations from thermodynamic equilibrium exist within the growth environment, and that the metastable phase is kinetically favored [8]. The general chemistry of microwave plasma enhanced chemical vapor deposition of diamond with H_2 , CH_4 , and O_2 as reacting gases is that H , CH_3 , C_2H , and OH , have been found to be the primary species generated by the plasma. At low CH_4 and O_2 concentrations the major exiting gas species include H_2 , CH_4 , C_2H_2 , H_2O , and CO [9]. In low pressure diamond growth, the methyl radical and acetylene have been identified as the major carbonic growth species. Using isotopic labeling experiments, Chu et al. [10] found that the methyl radical is the primary growth species. Accordingly, in the discussion only methyl radicals are considered, however similar arguments might be made for acetylene radicals. Martin and Hill [11], have reported that methyl radicals and atomic hydrogen have lifetimes in microseconds and seconds respectively. As previously indicated, the gas flows were maintained at constant flow rates during the deposition, and the microwaves were pulsed with approximately 50 percent duty cycles. Based on this understanding and upon the results of this experiment it is proposed that the extent of dissociation of the reactant gases determined the amount and nature of the deposit.

Films deposited with plasmas formed with nanosecond pulsed microwaves

were non-continuous and had little facet development. As previously noted the forward power rise times were on the same order as the pulse duration. During this period, the forward microwave power did not reach its maximum value limiting the dissociation of the incoming reactant gases. Scarsbrook et al. [5] reported that the dissociation of molecular nitrogen into atomic nitrogen did not reach its maximum concentration until 150 microseconds into the pulse, and indicated that reactant dissociation time within a plasma, may be dependent on its bond strength. Accordingly, it is estimated that the time it takes to dissociate molecular hydrogen into atomic hydrogen and reach its maximum concentration at the given microwave power, may be on the order of 75 microseconds. For nanosecond pulse periods, the generation of low concentration of active species resulted in very little crystal growth.

In the microsecond pulsed case, the increase of pulse duration to microseconds far exceeded the 40 nanosecond rise time of the microwave system. As a result, sufficient time was available for the microwave forward power to reach its maximum value during the pulse on-time. This allowed for an increase in reactant dissociation, greater than could be achieved in the nanosecond case. For the 5 microsecond pulse, the active species could still not reach their maximum concentration if dissociation times are in the order of tens of microseconds. Further, the microsecond pulse off-times are sufficiently long to allow the short lived methyl radicals, formed from the dissociation of methane, to recombine with atomic hydrogen. Methyl radicals must now be generated by hydrogen abstraction of methane with atomic hydrogen. This consumption reduces the number of atomic hydrogen formed [12]. However, when compared to the nanosecond case, the net increase in active species resulted in a decided film improvement over the nanosecond case.

In the millisecond case, rise time and dissociation time are small compared to the pulse on-time, and the reactants reach their maximum concentration for the given peak power. This maximum concentration of atomic hydrogen coupled with the concomitant increase of atomic hydrogen generated methyl radicals results in an increased growth rate for the film. In the millisecond case, because the generation rate of atomic hydrogen is significantly larger for millisecond than for either nano- or microsecond pulse periods, the amount of atomic hydrogen remaining after recombination is still higher than the other previous pulsed cases. However, the number of hydrogen atoms is sufficiently reduced to effect the growth rate and quality of the diamond film. Baseline films obtained with CW formed plasmas had growth rates and film quality that exceeded any obtained from pulsed-plasmas.

The extent of dissociation of the reacting gases is dependent upon the microwave forward power and the resultant plasma density, the time of dissociation, and the recombination rates. The plasma density is a function of the microwave forward power. Although the average power was approximately the same for both the CW and pulsed cases their peak power was not. Pulsed plasmas were operated at near 50 percent duty cycles and their peak power at 2.5 KW was double of that of the CW case. Due to the rise time, only the microsecond and millisecond pulses reached peak power during the pulse period. As a result the plasma density for these pulsed cases would be higher than CW cases. However, the plasma density would not have doubled, since the plasma density increases more slowly than the applied microwave power.

The time it took to dissociate the reactant gases impacted the nanosecond and microsecond pulsed cases, but was not a factor for either the millisecond pulsed or CW cases. Methyl radical recombination was a factor only for microsecond and millisecond pulsed cases. Atomic hydrogen recombination becomes significant only in the millisecond case. In this case, with the increased pulse off-time proportionately more atomic hydrogen recombines, and more significantly atomic hydrogen is not being generated. From the data reported by Martin and Hill [11], it is estimated that for the 5 millisecond off-time there is an 80 percent reduction in the ability to form diamond. For the experimental conditions used, CW plasmas produced a higher rate of reactant gas dissociation than any of the pulsed cases. As a result the growth rate and quality of CW films were higher than pulsed- plasma films.

As seen in Figure 2, the crystal facets increase in size and appearance as the pulse on-time increases. The size of crystal facets for vapor deposited crystalline films, whether by pulsed or CW plasma, is strongly dependent on the films' thickness as has been observed in cross-sectional SEM micrographs of the deposited diamond films. Crystal faceting can also be considered a measure of film quality. Harker and DeNatale [13], noted that an increase in the oxygen content of the reacting gases resulted in improvements in reactive etching rates, which increased the diamond crystallite size. Kawato and Kondo [9], experimentally determined that the quality as well as the growth rate of deposited diamond films are dependent on atomic hydrogen and oxygen. The possibility of depositing diamond layers with pulse on-times and non-diamond carbon during pulse off-times was considered. However, with subsecond pulse cycles and deposition rates at less than an angstrom per second, atomic layering could not be possible. As a result, it was concluded that diamond and non-diamond carbon are deposited simultaneously.

Because of the fixed composition of the incoming reactant gases, improvements in growth rates could in part be attributed to an increase in dissociation of the carbon precursor methane. However, due to the short lifetime of methyl radicals, the mechanism of hydrogen abstraction is needed to generate these radicals. Although oxygen has been shown to improve both the growth rate as well as the quality of low pressure, CVD deposited diamond film, it requires the presence of atomic hydrogen. Of the roles ascribed to oxygen by Spear and Frenklach [14], only that of promoting the gas phase production of hydrogen would apply to improving the growth rate of diamond films. It was first reported by Spitsyn et al. [14] that atomic hydrogen directly contributes to both the quality as well as the growth rate by stabilizing the diamond surface, preferentially etching sp and sp² bonded carbon from the growing surface, and activating the growth surface by hydrogen abstraction. The improvement in diamond film growth for increasing pulse periods which reached a maximum for CW grown films, would support the idea that these improvements were attributed primarily to increases of atomic hydrogen. For a given ratio of hydrogen and a carbon precursor such as methane, once diamond growth is initiated, further increases in the partial pressure of atomic hydrogen result in improved diamond growth rates and quality. This is in qualitative agreement with global mechanism proposed by Vandenbulcke et al. [16].

VI. SUMMARY AND CONCLUSIONS

Diamond films were grown in plasmas formed with microwaves that were modulated with a pulse generator. Films obtained with the use of cycle times in nanosecond, microsecond, and millisecond ranges with 50 percent pulse on-times were compared to baseline films which were obtained with a CW plasma. For the experimental conditions used, the diamond films' growth rates and quality improved with increasing pulse duration, and reached a maximum with CW generated films. This was attributed primarily to an increasing plasma on-time which resulted in a corresponding increase in the atomic hydrogen partial pressure at the growth surface.

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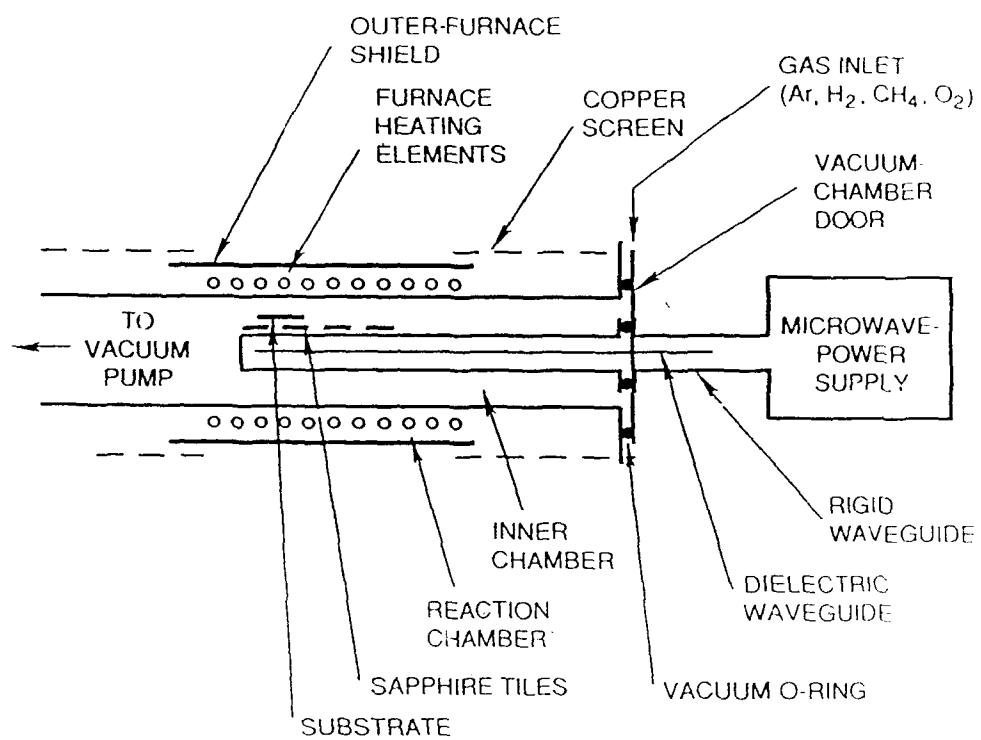


Figure 1. Schematic drawing of the pulse/CW plasma deposition system.

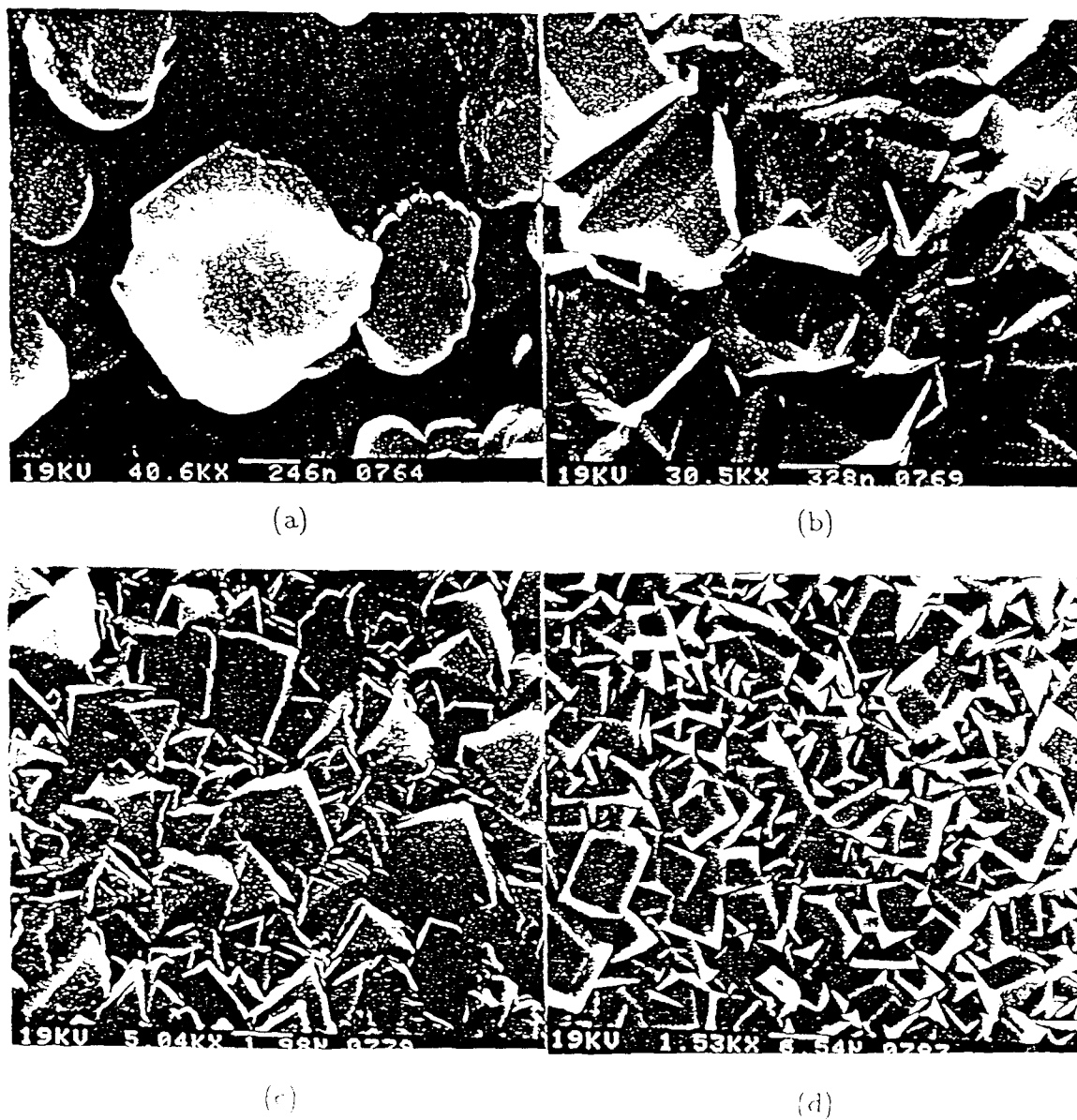


Figure 2 SEM microphotographs of deposited diamond films. (a) nanosecond pulsed plasma; (b) microsecond pulsed-plasma; (c) millisecond pulsed plasma; and (d) CW plasma

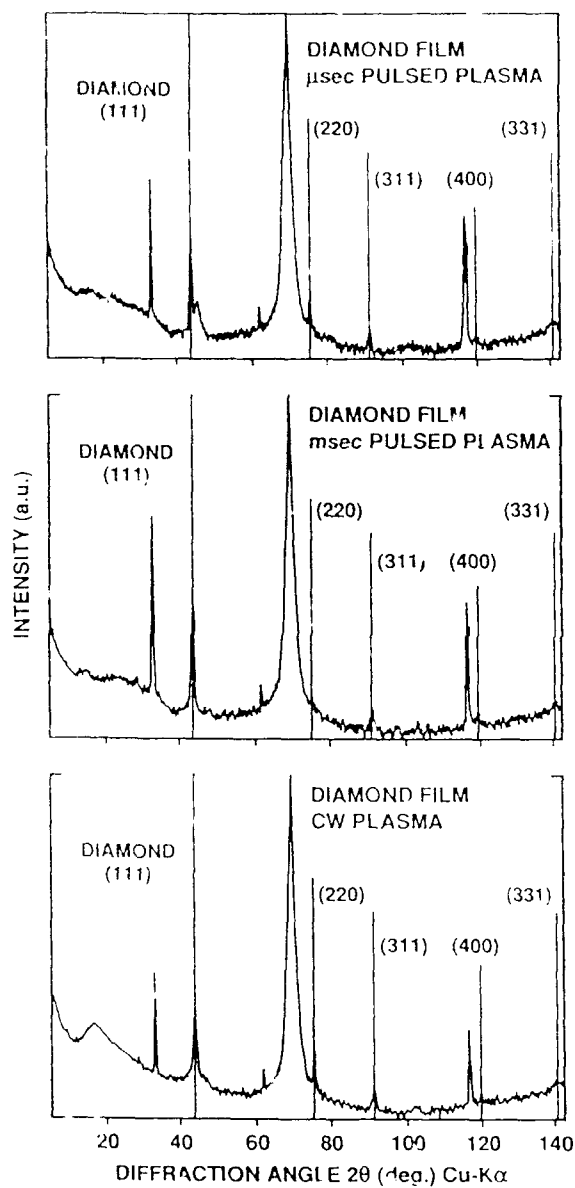


Figure 3. XRD pattern of microsecond and millisecond pulsed, and CW plasma deposited diamond film.

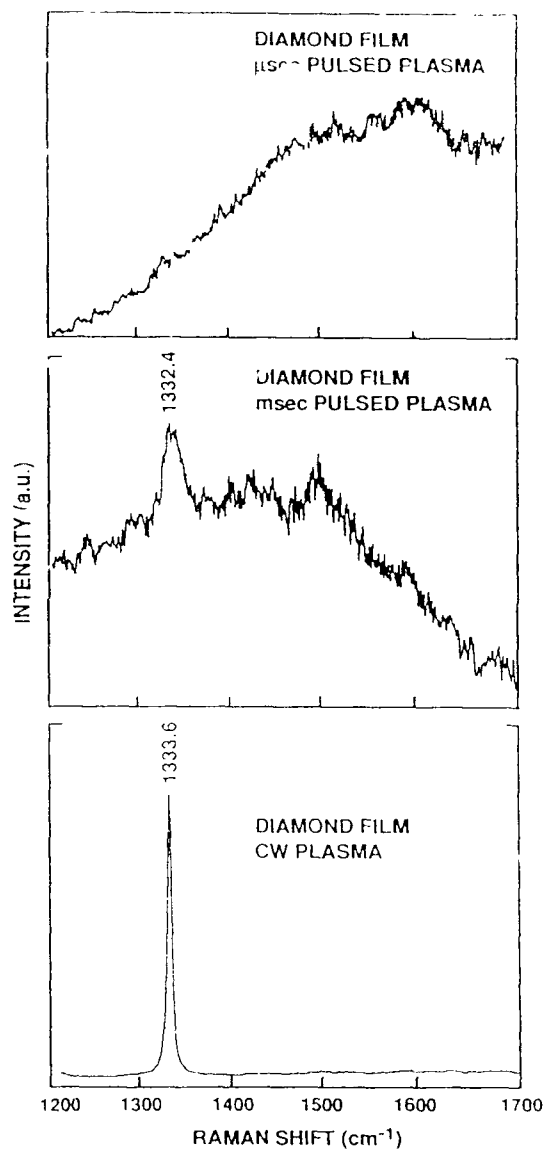


Figure 4. Micro-Raman spectra of microsecond and millisecond pulsed, and CW plasma deposited diamond film.

Semiconductor Films for High-Temperature Environments

M.E. Aklufi

A novel plasma-enhanced, chemical-vapor-deposition system has been developed. This system, which uses a dielectric waveguide to carry microwaves directly into a semiconductor furnace, forms planar plasmas within its hot zone. The system has been used to deposit high-quality diamond films on planar substrates of silicon, fused silica, sapphire, and silicon-on-sapphire.

INTRODUCTION

The civilian and military technological progress of the past 40 years has been driven by the electronic advances provided, in large part, by silicon semiconductor technology. As the material limitations of silicon are approached, the need becomes critical for other semiconductor materials that will enable us to maintain this rate of progress in the next century. One specific area of use for these semiconductor materials is in high-temperature environments. A potential semiconducting material, possessing unique physical and electrical characteristics with the ability to overcome the limitations inherent in silicon integrated circuits, is diamond. Diamond devices can operate at higher temperatures and are more radiation tolerant than are silicon devices. Diamond devices can operate at higher speeds and also dissipate more power than silicon devices.

The scarcity and high cost of diamond in bulk form has limited its use in semiconductor technology. However, promising work in the growth of diamond films under metastable conditions may provide the first practical step toward the goal of large-scale diamond integrated circuits. Of the published methods of forming diamond films, none has gained more attention than the microwave discharge chemical-vapor-deposition (CVD) technique (Kamo et al., 1983). This technique uses a rigid (hollow metal tube) waveguide to project the flow of microwaves at a frequency of 2.45 GHz through a fused-silica window of the deposition chamber. The microwave-generated plasma is formed at the substrate location within the deposition chamber near the microwave point of entry. A number of disadvantages exist with this approach. The plasma's spherical shape and gaussian density distribution, and the inability to locate the plasma other than near the microwave point of entry are of primary concern in planar semiconductor technology.

To circumvent these disadvantages, and at the same time provide a capability for scaling the system to accommodate large-area substrates, a planar-plasma deposition system has been developed. The primary difference from the Kamo system lies in the fact that this system uses a dielectric waveguide to carry microwaves directly into the reaction chamber.

This system is new, and the results of its initial use were published only recently (Aklufi and Brock, 1989).

METHOD AND RESULTS

A schematic of the system used in these experiments is shown in figure 1. The system consists of two basic sections, a gas-handling section and a microwave section. The reaction chamber is a 100-mm-inside-diameter (ID) fused-silica tube. This reaction chamber was placed in a resistance heated furnace. Mass-flow controllers were used to meter argon, hydrogen, carbon monoxide or methane, and oxygen gases and to feed the mixture through the vacuum-chamber door into the fused-silica reaction chamber.

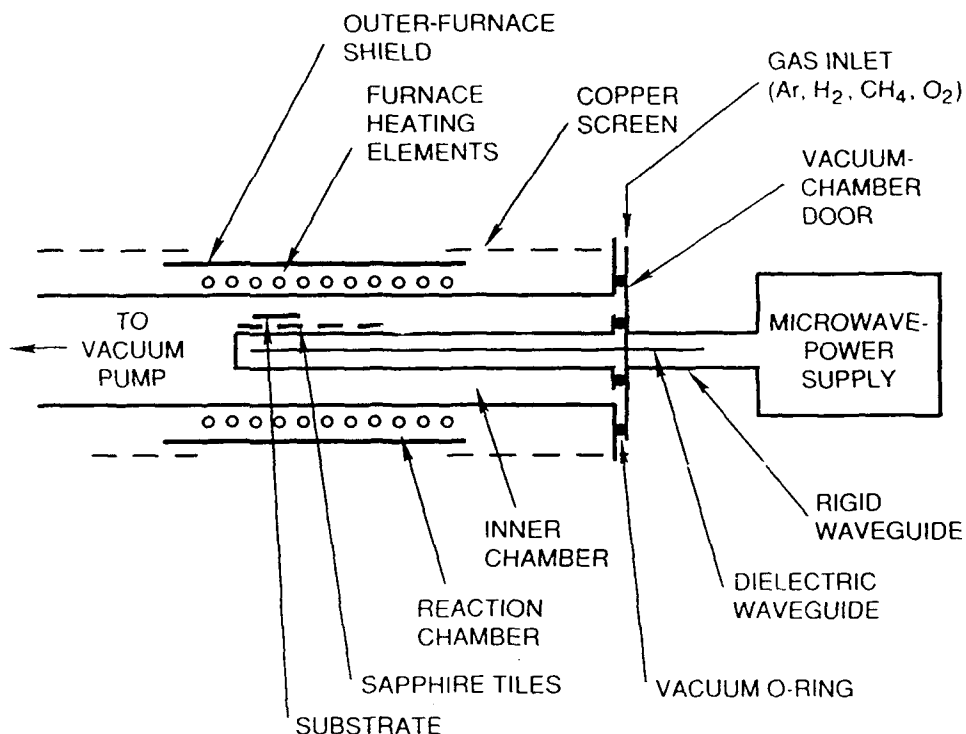


Figure 1. Schematic drawing of the microwave plasma-enhanced CVD system that uses dielectric waveguides to carry microwaves into the reaction chamber.

In the microwave section, microwaves in the frequency range of 7.36 ± 0.050 GHz, with a power range of 0 to 2.5 kW, were generated with a Hewlett Packard 8341B Synthesized Sweeper, a Hewlett Packard 495A Microwave Amplifier, and an Energy Systems Inc. 2.5 kW, low X-Band Klystron Power Amplifier. The microwaves were directed from the Klystron to the reaction chamber through rigid waveguides and a circulator. The microwaves were then transitioned into a 25-mm-diameter fused-silica rod. This rod was used as the dielectric waveguide. The portion of the dielectric waveguide located in the deposition chamber was inserted into an inner chamber that was maintained at atmospheric pressure. The outer chamber, which was operated at low pressure, was vacuum sealed with an o-ring at the vacuum-chamber door.

The depositions were normally performed on (100) n-type silicon, fused-silica, and (1102) sapphire substrates. To aid in the nucleation and reduce the time necessary to nucleate the diamond film, the substrates were seeded with diamond crystals that measured up to 2 μm in size. Typically, the substrates were placed horizontally on sapphire tiles that rested on the top of the inner chamber, just above the output end of the dielectric waveguide. The tiles, by covering the inner-chamber surface, minimized the potential contamination of the deposited film with silica chemically sputtered off this surface. After sealing the chamber and connecting the rigid waveguides, the deposition tube was evacuated to less than 100 millitorr by an Alcatel 2030 two-stage mechanical pump. Argon was then introduced into the reaction chamber and the pressure was maintained at 5 torr with a manual throttle valve.

With the system configured as shown in figure 1, the microwave cavity was defined, in part, by an arc-welded, copper mesh screen and a metal furnace shield that surrounded the 100-mm-diameter quartz tube. The Q of the system varied with the geometry of the microwave cavity. When the furnace was not used, the cavity was defined primarily by the surrounding arc-welded copper screen. The microwave power required to initiate the plasma with the furnace was about twice that required without the furnace. This result indicated that the Q of the microwave cavity was significantly reduced when the furnace was included. Microwave power was applied through the fused-silica dielectric waveguide into the deposition tube. When the furnace was included in this system, the plasma was typically initiated with the microwave power at 1.5 kW and at an argon pressure of about 5 torr. At this power, the plasma extended over the length of the inner chamber. The length of the plasma was controlled by the amount of microwave power and the amount and type of gas used. Once initiated, the plasma could be maintained over a wide range of gas pressure and microwave power. Within the constraints of this system, the plasma could be operated over the pressure range of 0.2 to 10 torr, and over a microwave-power range of 100 to 2,500 watts.

After the plasma was formed in argon gas, oxygen and then hydrogen were introduced. The deposition pressure was initially set with a throttle valve, and finally adjusted with a vernier-controlled metering valve. A microwave power was then selected to define the plasma region and the amount, if any, of heating required. Once the plasma was stabilized, either methane or carbon monoxide was introduced as the carbon precursor for the deposition of the diamond film.

Depositions were performed with and without the use of external heating. When a furnace was not used, the substrate was heated by the plasma and the microwave heating. Monitoring of the plasma and the extent of substrate heating was more readily accomplished when the reaction chamber was not inside the furnace. Figure 2 shows a photograph of the planar plasma. The plasma is seen located on the top and on the front surfaces of the inner chamber, which is located about the output end of the dielectric waveguide. This plasma was formed in a mixture of argon, hydrogen, carbon monoxide, and oxygen gases at 2.5 torr, with a microwave power of 1 kW at a frequency of 7.374 GHz. Substrate temperatures were measured with a Chapin Tec, Model ROS-5U two-color optical pyrometer. Typical substrate deposition temperatures were between 800°C and 1050°C. These temperatures could only be

measured approximately because of the difficulty measuring an exact temperature through the copper screen and the background emission of the discharge. The furnace allowed the initial substrate temperature to be accurately determined, as represented by the furnace temperature. However, any additional temperature rise due to the plasma and microwave heating could only be estimated from the amount of microwave power used. A fused-silica rod, inserted above the substrate in the furnace, acted as a window to observe the plasma.

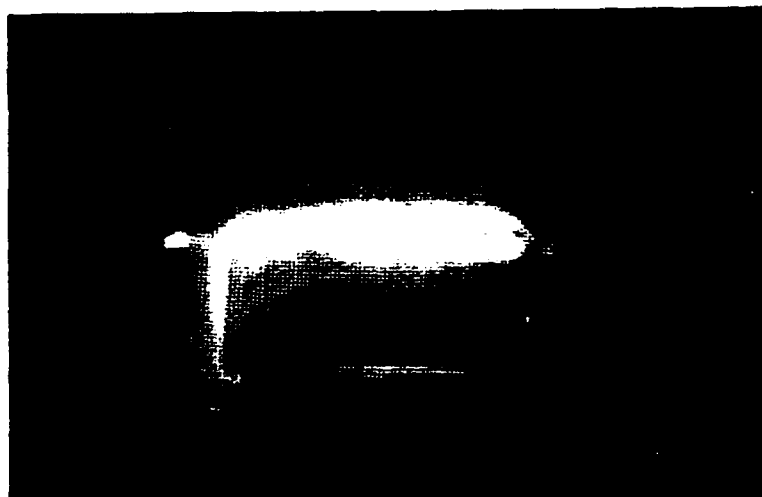


Figure 2. Planar plasma about the top and front surfaces of the inner chamber formed at the output end of a dielectric waveguide.

Initial diamond depositions were nucleated by using 0 to 0.25- μm , natural-cubic diamond seeds swabbed directly on the substrate surface. During these initial depositions, the substrates were placed directly on the fused-silica inner chamber. A silicon-on-sapphire (SOS) substrate with a 5- μm heteroepitaxial silicon layer was seeded in this manner. The SOS was deposited for 1 and 1/2 hours at a microwave power of 1.2 kW, with a gas flow consisting of 141 cc/min of argon/0.5% oxygen mixture, 37 cc/min hydrogen, and 4 cc/min carbon monoxide, at a pressure of 2.4 torr. Chemical sputtering of both the silicon epitaxial layer and the inner chamber was noted. The top surface morphology of this deposit was examined with an ISI DS130C Scanning Electron Microscope (SEM). The deposition was limited to the small diamond-seeded region and resulted in the platelet growth shown in the micrograph of figure 3a.

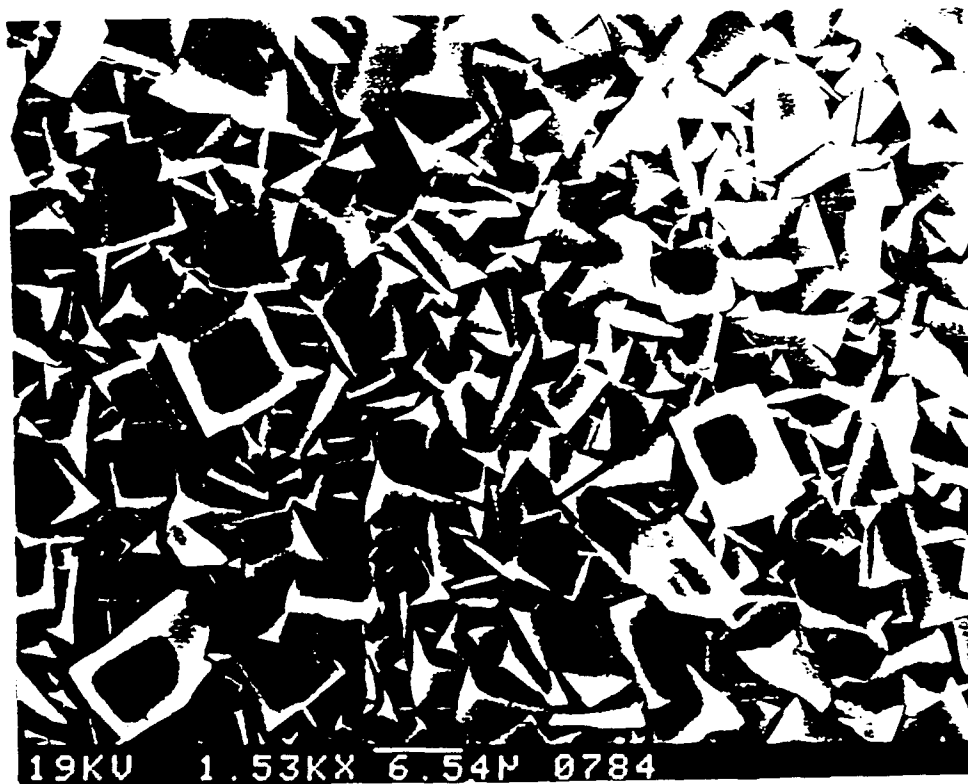
To obtain a more uniform seeded region and simultaneously expand the area of deposition, the entire deposition surface of the substrate was abraded with 0- to 2- μm , natural-cubic-diamond powder. After the surface was abraded, high-pressure nitrogen gas was used to blow loose particulates from the surface. In addition, sapphire tiles were placed on the inner chamber, in the region of the plasma, to protect the inner chamber from chemical sputtering during the deposition. A silicon substrate, prepared in this manner, was deposited for seven hours at a microwave power of 1.5 kW, and gas flows of 100 cc/min argon, 100 cc/min hydrogen, 0.5 cc/min oxygen, and 0.5 cc/min methane at a pressure of 6 torr (figure 3b). The deposit was made up of highly faceted individual crystals that displayed both square {100} facets and triangular {111} facets typically found on cubic crystals. The deposition rate, calculated from the film thickness, was 1.5 μm per hour. This deposition procedure was repeated for fused-silica and sapphire substrates.

A Rigaku Rotaflex RU 200B X-ray diffractometer (XRD) was used to determine the structure and nature of the deposits. Film excitation was produced with Cu-K α X-rays. X-ray diffraction patterns for deposits on silicon, fused silica, and sapphire are shown in figure 4. Attempts to obtain an XRD of the small deposited region shown in figure 3a were unsuccessful. The stick figures of the standard powder pattern of cubic diamond, shown in red, define the location and relative intensity of the most prominent cubic-diamond crystallographic planes (i.e., (111), (220), (311), (400), and (331)) within the diffraction angle of 2θ that lies between 0 to 140 degrees. The intensity of the diamond peaks are lower for thinner films. Sharp peaks not located at the stick figures are those of the crystalline substrates (i.e., silicon and sapphire). The fused-silica substrate is amorphous and exhibits only a broad band. Of particular interest is the deviation between the powder-pattern stick-figure intensity ratios and that of the intensity ratios for the deposited diamond films. These differences indicate that the deposited diamond films exhibit pronounced texture (i.e., preferred orientation).

Raman spectroscopy is an effective nondestructive technique for evaluating deposited carbon films. Carbon gives a Raman spectrum between 1300 and 1600 cm^{-1} . A very high-intensity peak ratio between sp² graphitic bonding and sp³ diamond bonding allows the qualitative detection of small amounts of graphitic carbon that may be present.



(a). Hexagonal-diamond platelets.



(b). Cubic-diamond crystals.

Figure 3. SEM micrographs of diamond films.

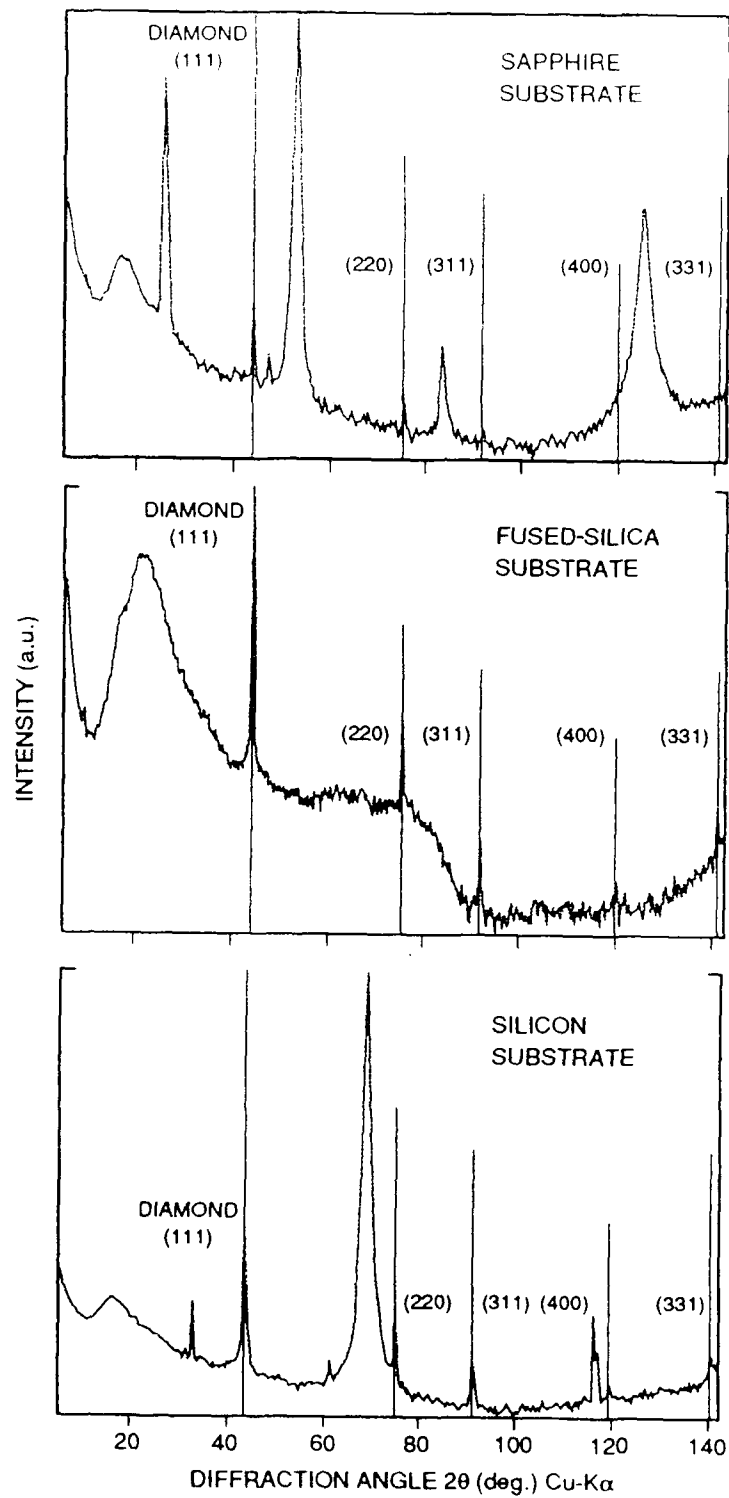


Figure 4. XRD pattern of diamond films on silicon, fused-silica, and sapphire planar substrates.

The Raman spectra shown in figure 5 was generated by Instruments SA on their Raman Microprobe S3000 spectrophotometer. Excitation was provided with the 514.5-nm line of an argon ion laser. A spectrum for a single cubic crystal of natural diamond, included for reference purposes, gave the characteristic sharp diamond carbon peak at 1332.5 cm^{-1} . The Raman spectra of a single crystal from a cubic-diamond film deposited on silicon shows a sharp diamond carbon peak at 1333.6 cm^{-1} . Stressed diamonds have been found to exhibit wavenumber shifts (Sharma et al., 1985). The small wavenumber shift noted in this deposited diamond film is attributed to the internal stress within the diamond film generated by the substrate on the film.

The platelet structure (figure 3a), was probed with the Raman Microprobe's $1\text{-}\mu\text{m}$ -diameter beam. This beam produced the Raman spectra with a peak at 1318.6 cm^{-1} shown in figure 5. Synthetic hexagonal diamonds, produced by the shock-loading technique, have generated Raman spectra with wavenumbers between 1315 and 1326 cm^{-1} (Knight and White, 1989). This large peak shift could not be attributed solely to film stress, because similar peak values were also obtained with swabbed seeded regions on silicon substrates. As noted above, deposits on silicon substrates have shown only small peak shifts. None of the Raman spectra in figure 5 shows any evidence of nondiamond carbon peaks either between 1340 and 1360 cm^{-1} , or 1550 and 1595 cm^{-1} . The hexagonal Raman spectra has a low signal-to-noise ratio in addition to its luminescent background. This is due to the fact that the intensity of Raman peaks are directly proportional to the film's thickness. Because the Raman spectra of cut diamonds sometimes show a satellite peak at 1319 cm^{-1} , in addition to the primary 1332 cm^{-1} peak, the plasma conditions are hypothesized to have, in part, converted the cubic crystal seeds to hexagonal diamonds.

Secondary Ion Mass Spectroscopy (SIMS) is a sensitive technique for determining the presence of impurities, with detection limits up to parts per trillion (ppt. = 10^{-12}). A Perkin-Elmer model 6300 Secondary Ion Mass Spectrometer with a cesium ion beam was used to examine the surfaces of a silicon substrate and a diamond film deposited on a silicon substrate. The negative ion SIMS survey spectra of the near surface analysis of these surfaces are shown in figure 6. The primary constituents found in the silicon-surface analysis are silicon, oxygen, and compounds thereof. The native oxide formed on the surface of the silicon is a source of oxygen in this spectrum. In the case of the diamond film, the primary constituents are carbon, hydrogen, and compounds thereof. The higher ratio of H to OH_x for the diamond film indicates some of the hydrogen is from the hydrogen gas used in the plasma deposition of the diamond film. Fedoseev et al. (1984), experimentally determined that atomic hydrogen plays an important role in enhancing the growth of diamond and reducing or eliminating the codeposition of nondiamond carbon. The role of atomic hydrogen is to form C-H sp^3 surface bonds and to activate growth surfaces by hydrogen abstraction from the C-H stabilized surfaces. In both cases, water vapor also contributed to the H and OH_x signals.

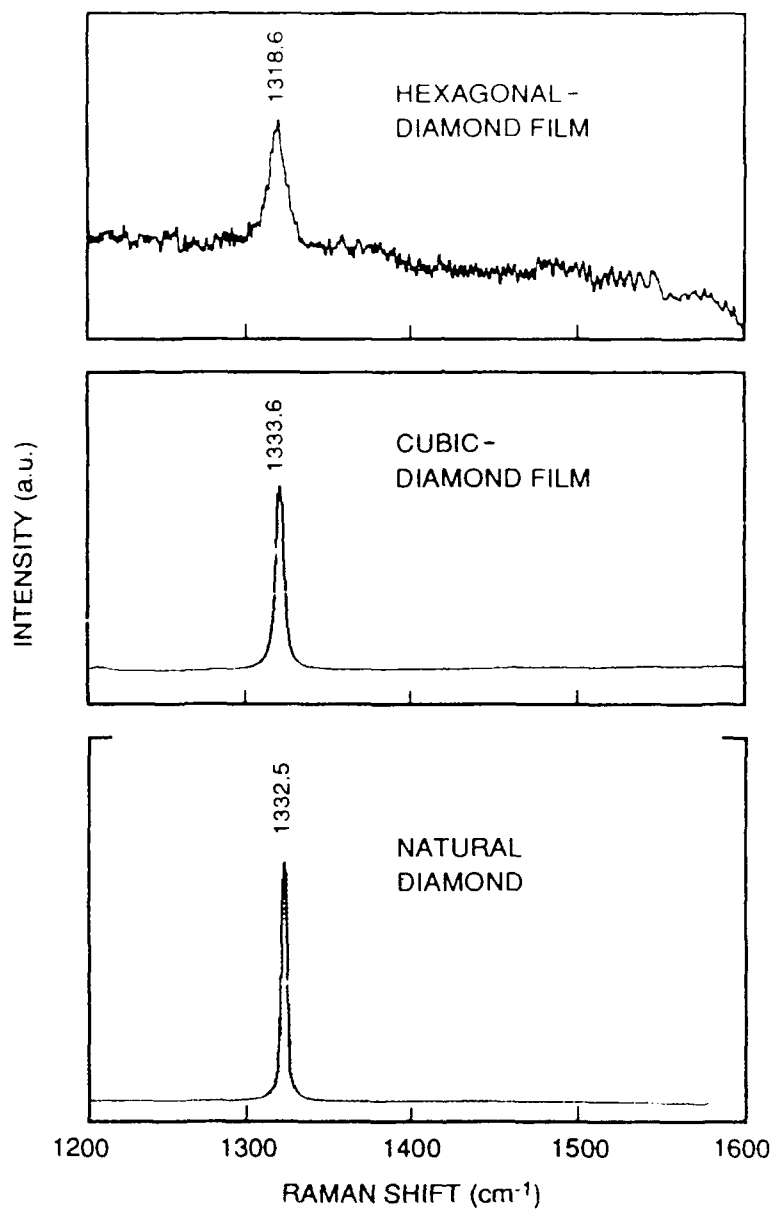


Figure 5. Micro-Raman spectra of natural cubic diamond, cubic-diamond film, and hexagonal-diamond films.

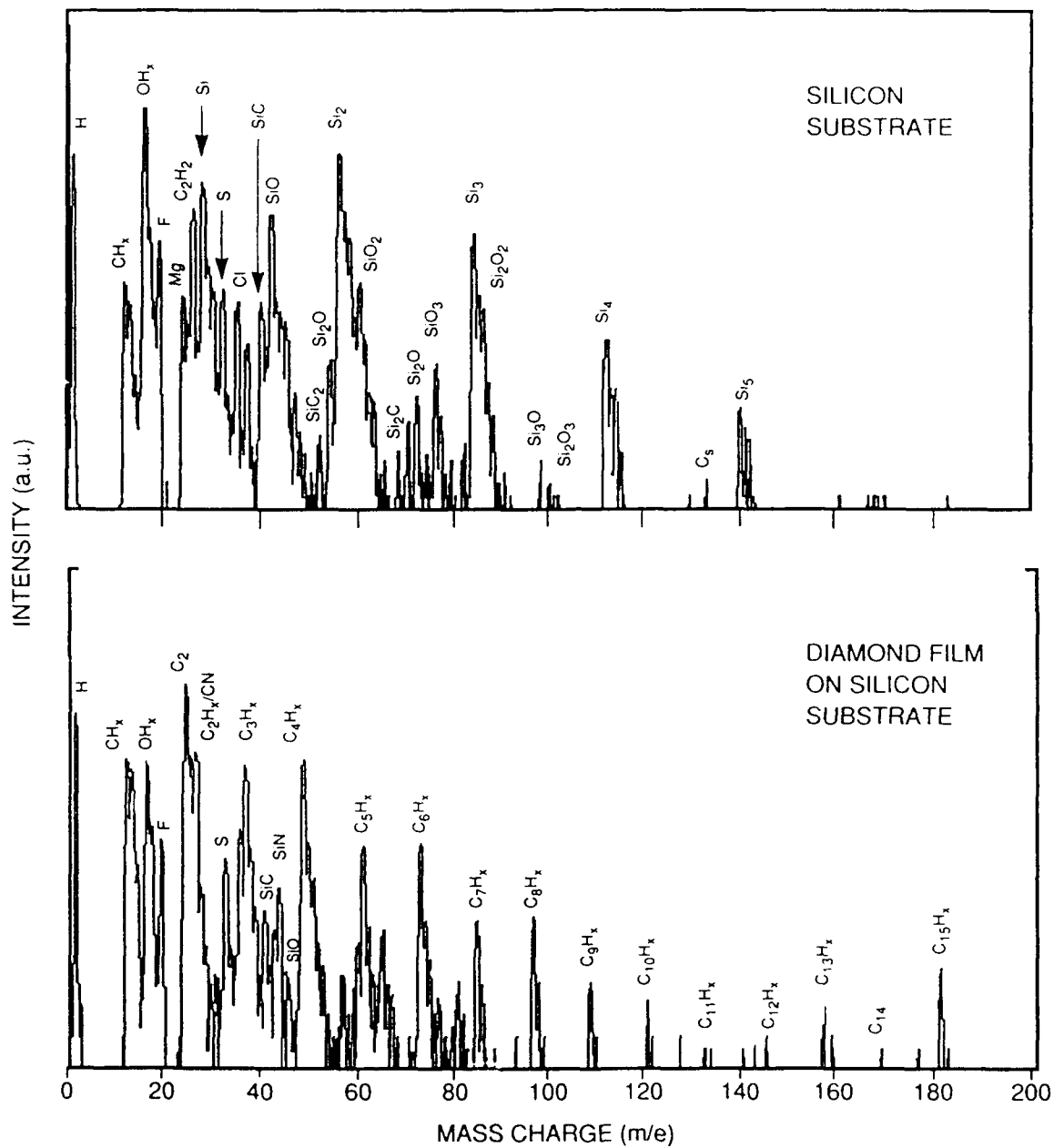


Figure 6. Negative ion SIMS spectra of the near surfaces of a silicon substrate and of a diamond film deposited on a silicon substrate.

High-quality diamond films can also exhibit the same brilliance typically seen in diamond jewelry, provided that the diamond crystals within the film have well-defined facets. This brilliance can be seen by using an optical microscope equipped with a Nomarski objective (figure 7a). Diamond-crystal growth under CVD techniques usually have the fewest externally imposed constraints. If no significant merging of well-defined individual crystals has taken place, a cubic diamond can display only its slowest growth planes. This can be seen in the micrograph of figure 7b, where diamond tetrahedral crystals are defined by a family of (111) planes. Crystals can also grow in an accelerated manner such as in dendritic growth. These growths typically have branching structures with significantly larger crystals than found in more orderly growth. A micrograph of such a structure, grown up from the diamond-seeded substrate region, is shown in figure 7c.

CONCLUSION

A planar-plasma, chemical-vapor-deposition system has been developed to deposit diamond films. High-quality diamond films have been deposited on silicon, fused-silica, and sapphire planar substrates. These developments may signal the first practical step towards the goal of forming large-scale, diamond integrated circuits for use in areas such as high-temperature environments.

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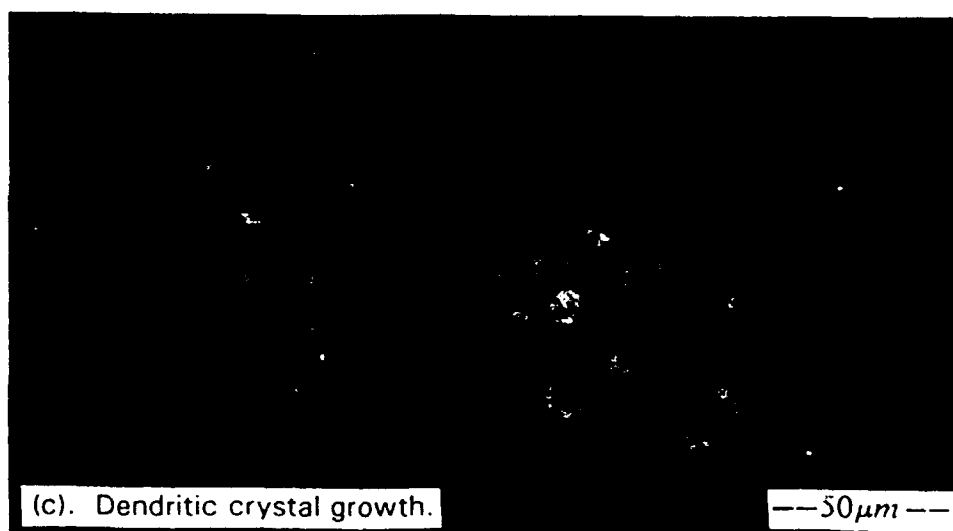
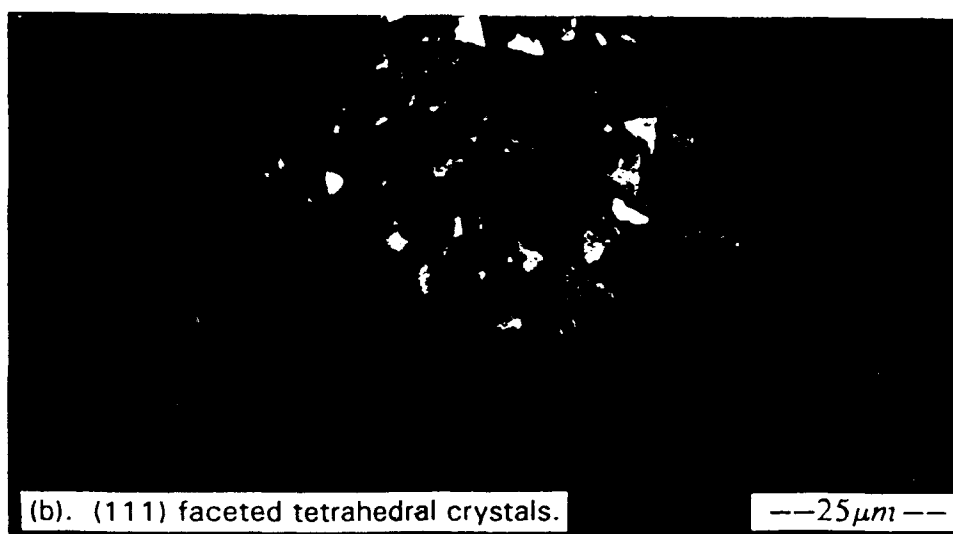
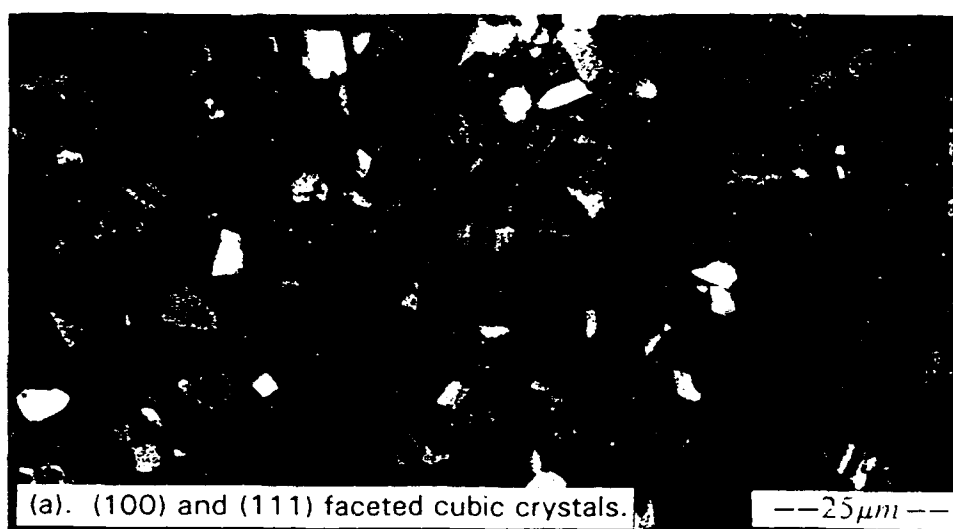


Figure 7. Nomarski optical microscope micrographs of diamond films.